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HIGH-PRESSURE SMALL VOLUME PUMP

The present invention refers to pumps according to the preamble of claim 1. Furthermore, the invention refers to adjusting methods and to applications of such pumps.

Pumps capable of delivering smallest volumes of liquids under high pressures with minimum losses, minimum pulsation and a correspondingly accurate, determined flow rate are required particularly for HPLC (High Performance Liquid Chromatography). Current flow rates today range up to approx. 5 ml/min (milliliters per minute) at an operating pressure of the chromatography column of e.g. 100 bar, while the gradient capability extends down to 100 µl/min (microliters per minute). However, pressures up to 700 bar are already being applied, and there is also a tendency to use volumes as small as 1 µl/min and thus smaller flow rates. Therefore, in such applications, losses below one microliter are at least noticeable or even unacceptable.

A current construction comprises two positive displacement pump units arranged in series. The fist unit is the feed pump, which aspirates the liquid at low pressure, e.g. at ambient pressure, and delivers it to the second unit, the storage pump, at operating pressure. The storage pump essentially operates in a push-pull relationship with the first unit. It delivers a liquid flow while the first unit aspirates the liquid and stores the surplus while the first unit is expelling the working medium at the operating pressure. This allows achieving a regular flow with low pulsation.

Especially in high-grade pumps for this application, the pistons are made of mechanically resistant materials, more particularly ceramic (preferred), crystalline and/or mineral

materials, which are guided in stone bearings, i.e. ruby, sapphire, synthetic corundum, or ceramic bearings. Tightness is ensured by piston seals that are open towards the working volume. Thus, since the working medium under pressure accesses the outside of the sealing lip, the latter is pressed against the piston surface by the working pressure, thereby providing the corresponding sealing effect by itself. In order to ensure the required pressure resistance and chemical inertness, the parts in contact with the working medium are made of high-grade materials, metals, and precious stones. Thus, the use of titanium is current practice, for example. The pistons are driven by camshafts acting on the rear end of the pistons in combination with resilient restoring elements.

However, on account of the high pressures and of the required accuracy, the compressibility of the liquids becomes noticeable, so that a pump of this kind can be adjusted for minimum compressibility only at a given pressure by mutually adjusting the sequences of movements of the two pump units. An additional difficulty is that the dead space of such pumps is relatively large compared to the dispensing volume of approx. 10 to 50 microliters per stroke in gradient applications, so that the dead space may even be greater than the dispensing volume. The large dead space is mainly a result of the minimal distance of the piston from the bottom of the displacement chamber and of the piston seal. The minimal distance is necessary to prevent the piston from hitting the bottom in spite of manufacturing and mounting tolerances: such a collision may damage the piston, the bottom, or other parts of the pump. Regarding the piston seal, it appears that in the mounting position where the seal is open towards the working medium, the seal is filled with the working medium, which requires relatively large volumes in the order of the dispensing volume. Thus,

the dead space as well as minimal leaks, which are not even detectable visually on account of the small volumes, will impair the dispensing quality of the pump, particularly the uniformity of the adjusted flow rate and the absence of pulsation.

In particular, the dead space affects the gradient capability, i.e. it determines the minimal dispensing rate at which a working medium of changing composition can still be delivered by the pump without being substantially mixed. A large dead space contains correspondingly large quantities of the working medium that also have to be exchanged to avoid mixing in gradient operation.

Furthermore, the pumps are subject to aging, thereby requiring maintenance. Due to the stringent requirements especially in the assembly, this must be done by a specialist.

Suitable pumps are e.g. known from DE-A-43 08 467. The particularity of these pumps is that they are composed of disk-shaped functional blocks that are clamped together in a clamping device. The fact that the junctions extend between the blocks eliminates the need for external connecting ducts.

However, an inconvenient in this arrangement is that the pump must be assembled extremely carefully in order to achieve the required tightness since the tolerances add up. Therefore, inter alia, two ruby guides must be provided in the pump blocks to achieve a precise guidance of the pistons in the displacement chamber: a direct contact of the piston with the wall of the chamber must be avoided because of the resulting abrasion that may e.g. distort the result of the HPLC and destroy the piston seal.

In addition, it is generally necessary to dismount the entire assembly for maintenance operations. Finally, this pump has a considerable dead space.

It is therefore an object of the present invention to provide a pump of this kind that reduces the influence of construction tolerances on the dispensing quality.

Another object consists in controlling and/or reducing the influence of the dead space.

Pumps of this kind allowing to attain at least one of the above-mentioned objects are indicated in the device claims. Methods for the operation of the pumps and applications thereof are the object of additional claims.

Thus, a main aspect of the invention is to provide the possibility of adjusting the dead space and furthermore a general reduction thereof. One measure to this effect is a construction of the displacement chamber and/or of the piston that allows the adjustment of a minimum dead space or of a dead space resulting in an optimum behavior of the pump at the desired operating pressure. It is therefore suggested, on one hand, to make the total length of the piston adjustable by dividing it into the proper piston and a piston rod. The connection between the piston and the piston rod is adjustable in length, thereby allowing an adjustment providing a minimum distance of the piston from the bottom of the displacement chamber. The distance may even be set to zero if in order to avoid damages, the bottom of the chamber is formed of an insert that is sufficiently incompressible under operating pressure but nevertheless capable of yielding enough to prevent damages when hit by the piston. Another approach consists in providing an

opposed piston whose front end essentially forms the chamber bottom, thereby making the chamber bottom adjustable.

Furthermore, novel constructions of the seals between the piston and the displacement chamber also provide a reduction of the dead space. The classic piston seal comprises a spiral spring enclosed in the piston seal and surrounding the sealing lip. Particularly the interior of the spiral spring causes a large dead space.

In a first variant, a laterally open spring element is suggested. The aperture allows a filling body to be inserted in the spring element such that the major part of the cavity within the spring element is filled. In the second variant, the spring element is essentially in the form of a band-shaped element surrounding the sealing lip. Preferably, the latter is a spiral of a spring-elastic material, particularly metal. The flat shape of the spring element allows a small cross-section of the internal wall of the displacement chamber also in the area of the seal, thereby keeping the dead space small.

Furthermore, the reduction resp. adjusting capacity of the dead space also counteracts the effect of manufacturing tolerances.

Another problematic zone with regard to tolerances in assembly consists in small misalignments or angular deviations of the connecting elements required at the inlets and outlets of the pump units, i.e. at the access points of the working medium. To this effect, in the known embodiment, a connecting piece in the form of a so-called cartridge is inserted between the connecting element and the access. Such a cartridge may essentially have the form of a pipe section (coupling sleeve) or e.g. comprise a check

valve ("valve cartridge"). According to another aspect of the invention, it is suggested that the involved pairs of surfaces are designed as a combination of a cambered (convex, spherical) and a concave conical surface. A misalignment between the medium inlet and the connecting element results in a slightly canted fit of the cartridge. The mentioned design nevertheless provides a circular contact line and a regular contact pressure. Besides, the involved pairs of surfaces may be formed not only on the mentioned parts but also on the corresponding part and on a sealing body (a capsule). In this case, the cambered surface will preferably be provided on the capsule.

The invention will be further explained by means of an exemplary embodiment and with reference to figures, where:

Fig. 1 shows a longitudinal section through a pumping head of the invention according to I-I in Fig. 2;

Fig. 2 shows a sectional view according to II-II in Fig. 1;

Fig. 3 shows detail III in Fig. 1: first embodiment of a piston seal (enlarged);

Fig. 4 shows detail IV in Fig. 1: second embodiment of a piston seal (enlarged, sectional view);

Fig. 5 shows the spring in the seal of Fig. 4 (sectional view);

Fig. 6 shows an enlarged detail of Fig. 7: schematic illustration of a misalignment;

Fig. 7 shows an enlarged detail of a junction between the displacement chamber and a connection;

Fig. 8 shows a variant of a seal on a connection in a strongly enlarged sectional view;

Fig. 9 shows the design of the sealing surface in an enlarged partial view IX of Fig. 7;

Fig. 10 shows a variant of the sealing surface of Fig. 9;

Fig. 11 shows a sectional view of a seal for an opposed piston;

Fig. 12 shows a partial section of a variant of the connections;

Fig. 13 shows a longitudinal section of a connecting assembly in the straight state.

Figs. 1 and 2 show sectional views of head 1 of a HPLC pump designed according to the invention. The elements that are not represented (driving units with cam disks etc.) are realized according to the prior art. The piston assemblies for feed pump device 3 (feed pump) and storage pump device 4 (storage pump), replacing the undivided pistons of the prior art, are formed of respective pistons 7, 8 and piston rods 11, 12. The piston rods are guided in high-grade linear guides in the enclosure of the driving unit, more particularly in linear ball bearings (not shown).. Bearings of this kind are known per se in the art.

At the rear ends of pistons 7, 8, respective sleeves 15, 16 are fixedly fitted on hard material bars 19, 20, i.e. bars

of a mechanically resistant material (e.g. ceramic). Sleeves 15, 16 are closed at their rear ends. In order to precisely determine the total length of pistons 7, 8 (distance between the front ends of hard material bars 19, 20 and rear ends 22, 23 of sleeves 15, 16) in assembly, respective steel balls 25 (e.g. of hardened steel) are first inserted in bores 26 and the corresponding hard material bar 19, 20 is pressed into the collar. Balls 25 provide a defined contact in the center of the hard material bars, on one hand, and on the other hand, an annular contact on the bottom of bores 26 whose shape is conical due to the shape of the tips of usual drills.

Sleeves 15, 16 are seated in location holes 28 in the ends of piston rods 11, 12. In the case of the piston 8 of storage pump 4, a spring 32 is inserted in a smaller location hole 30 in the bottom of location hole 28, the free end of the spring resting on the bottom 23 of sleeve 16. Each one of piston rods 11, 12 is surrounded by a set collar 36. Each set collar 36 comprises a set screw 38 in a thread 39, the end of the screw contacting sleeve 15, 16 through a bore 40 in piston rod 11, 12. The pistons 7, 8 are thus capable of being locked in the respective piston rod by fastening screw 38. Screw 38 of storage pump 4 is accessible from the outside through an aperture 42 in the enclosure of pump head 1.

In contrast, in the feed pump, bore 31 in piston rod 11 is internally threaded to receive a threaded stem 33 attached to sleeve 15. A precise adjustment of the piston length is thus possible through a rotation of threaded stem 33. Generally, however, to prevent an undesired change in length, a locking device is required here too, e.g. a set collar 36 with a set screw 38. In this embodiment, the adjustment of the dead space in the assembled state is

obtained by varying the displacement chamber, for which purpose a solution will be indicated below.

Both hard material bars 19, 20 extend into the proper displacement chamber 47 through a conventional piston seal 44, a stone bearing 46 (e.g. of synthetic precious stone such as ruby) and finally through a piston seal according to the invention that provides a reduced dead space. Chamber 47 is formed of a highly resistant and chemically inert material, e.g. of titanium.

Outlet 112 of feed pump 3 is connected to inlet 115 of storage pump 4 by a known flexible conduit 114 having a small internal volume. Conduit 114 is tightly fastened to the connections by screwed joints known per se.

The dispensing piston is shown with a first embodiment 48 of a piston seal of the invention that is illustrated on an enlarged scale in Fig. 3. It is essentially formed of a sealing body 50 of essentially L-shaped cross-section, one leg 52 of which forms a sleeve-shaped sealing lip in which hard material bar 19 resp. 20 of a piston 7 resp. 8 is insertable. The sealing lip is surrounded by a spring 54 in such a manner that the spiral turns themselves wind around the sealing lip. As appears in Fig. 1, this allows a relatively narrow design of internal wall 56 around seal 48 as compared to the environment of the conventional piston seal 44, thereby providing a considerable reduction of the dead space. This is illustrated by the following data of an embodiment of a pump having a dispensing volume of 23 microliters: dead space of a conventional piston seal itself: 18 microliters; dead space of the additional space in front of the piston seal inside the displacement chamber: 11 microliters; total dead space of a piston seal of the conventional type: 29 microliters. The described seal of

the invention thus allows a reduction to approx. 20 %, i.e. approx. 6 microliters. The dead space is therefore reduced to a fraction of the dispensing volume.

Displacement chamber 47 of feed pump 3 is open at the bottom and closed by means of an opposed piston 58 whose front end forms the (movable) bottom of the displacement chamber. Opposed piston 58 is also made of titanium. Opposed piston 58 extends through a sealing bushing 60 retained by a clamping sleeve 62 in an enlarged portion 64 of displacement chamber bore 57. It is also possible to provide a screwed attachment both of sleeve 62 in enlarged portion 64 and of opposed piston 58 in sleeve 62 to allow a displacement of the opposed piston by rotation thereof and thus a variation of the displacement chamber volume.

Fig. 11 shows a seal 64 of the prior art that may be inserted instead of sealing bushing 60 and results in a reduced dead space. Since opposed piston 58 is not moved in operation and only rarely otherwise, the requirements with regard to this seal are substantially less stringent. Seal 64 comprises a seal body 65 with a sealing lip 66 that is pressed against opposed piston 58 (not shown). The contact pressure is initially provided by embedded O-ring 67 and in operation by the internal pressure of the pump acting upon O-ring 67 and on the sealing lip. Possible materials for the seal body are pressure-resistant materials that are chemically inert under the operating conditions, such as PTFE, in particular. A corresponding elastomer will be selected for the O-ring, e.g. KALREZ (DuPont). Seals of this kind are known <u>per se</u>.

In the storage pump, another embodiment 70 of a piston seal according to the invention is illustrated. An enlarged view of the applied piston seal 70 is shown in Fig. 4 and the

special spring element in Fig. 5. Sealing element 72 of the piston seal is C-shaped in cross-section, and so is spring element 74. A thickened or cambered portion 75 is formed at the end of internal sealing lip 73. The internal surface 76 of spring element 74 and its curved portion 77 are divided by multiple slots 79. Depending on the desired rigidity, the slots also divide external surface 81, the rigidity decreasing with the width of remaining lands 82. Curved portion 77 describes an angle that is a little smaller than 180°, so that the internal surface is slightly biased inwards. Thus, when spring element 74 is inserted in sealing element 72, a prestress of sealing lip 73 is achieved.

According to Fig. 4, spring element 74 is arranged in sealing element 72 with the cross-sections extending in parallel, and an annular filling body 83 is inserted in the resulting annular gap. The filling body consists of a material that is chemically inert to the working medium and substantially incompressible under working pressure. The filling body is so dimensioned that it largely fills out the interior of the spring element, i.e. at least half of it, preferably at least 90% and more preferably at least 99%. Basically, is should be as voluminous as possible, however without reducing the spring action of the spring element below the required level.

By filling out the empty volume, the dead space caused by the seal is substantially reduced while maintaining the same mounting dimensions as in the case of a conventional piston seal.

The storage pump also comprises an arrangement for adjusting the dead space that includes the adjusting device between piston 8 and piston rod 16 as well as an insert 87 in

displacement chamber 89. The material of insert 87 is chosen such that a contact between hard material bar 20 and insert 87 is possible without causing damages. In particular, a material will be chosen that is inert to the working medium and substantially incompressible under operating pressure while still being slightly deformable by the mechanically resistant material. It will be noted in this context that the circumference of the front ends of hard material bars 19, 20 is rounded to avoid damages of the seals and guides when they are inserted in the displacement chambers. The material of insert 87 is capable of a certain adaptation to this rounded edge, thereby additionally reducing the dead space.

Displacement chambers 47, 89 are located in bores of a pump block 91. For a correct alignment to laterally arranged access bores 92, displacement chambers 47, 89 comprise a groove 93 in which a pin 94 engages.

Displacement chambers 47, 89 are followed by an extension ring 95 which is fixed in block extension 96 by a threaded ring 97. Block extension 96 is screwed to block 91.

All parts that are exposed to the working medium are made of materials which are inert to the working medium. In addition, if they are also exposed to the operating pressure, they must resist the pressure without noticeable compression or deformation. For parts of the enclosure such as displacement chambers, cartridges, connections, but also for metallic sealing membranes, titanium has been found to be a particularly suitable metal. Generally, the pressure resistance of the mechanically resistant material of the pistons is unproblematic. As the case may be, care must be taken of the chemical inertness, although it is generally ensured as well. For those parts which must have a certain

elasticity (insert 87, body of the piston seals, seals, etc.), an elastomer, preferably the synthetic material PTFE (polytetrafluorethylene) may be used, particularly PTFE reinforced with graphite fibers, which offers an increased wear, pressure, and temperature resistance. Particularly for seals, PEEK (polyetherether ketone) is possible, too.

Finally it will be mentioned that the feed pump and the storage pump may also be identical in design. Thus, in particular, both pumps may be provided with the same inventive piston seals of either type.

In a further preferred embodiment, instead of an opposed piston, the feed pump may comprise a closed displacement chamber with an insert 87, i.e. it may be designed like the described storage pump and conversely, the storage pump may be designed like the described feed pump. It is thereby possible to adjust the dead space of the feed pump to nearly zero, which is optimal in almost all operating conditions. A subsequent adjustment of the opposed piston in the storage pump allows to minimize the pulsation, i.e. to adjust the pump to the working pressure and to the compressibility of the working medium.

As the storage pump operates under constant pressure and is therefore subject to less stringent requirements, measures for reducing resp. adjusting the dead space in its displacement chamber may alternatively be omitted. In applications with particularly low quality requirements, on one hand, it is even possible to use a conventional piston seal in the storage chamber, and on the other hand, some measures for reducing the dead space may also be omitted in the feed pump.

The adjustment of a determined dead space at the bottom of the displacement chamber, or in the extreme case of a dead space reduced to nearly zero, is always effected by first moving the respective piston to the upper dead center, i.e. by moving the drive to the position of maximum penetration of the piston into the displacement chamber, while the corresponding set screw is loosened. In the embodiment provided with an insert 87, the hard material bar of the piston now contacts insert 87. Set screw 38 is tightened, whereby the dead space is adjusted to minimum.

If an opposed piston is provided, the dead space may subsequently be enlarged to a desired amount by retracting the opposed piston.

A further basic aspect with regard to the quality of a pump of this kind is tightness. It will be noted that minimal leakage, which is not detectable externally due to the small volumes of e.g. substantially less than 1 microliter, may already influence the result. In this respect, the sealing of the various connections against the displacement chambers constitutes a problem of utmost importance.

To this effect, it is known practice to connect the connecting elements directly to the sealing surfaces of the displacement chambers by means of cartridges 101, 102. As usual, the cartridges may simply represent passages (see Fig. 7, cartridge 101), or e.g. check valves 102 as provided according to Figs. 1 and 2 at the inlet 111 and outlet 112 of the feed pump.

However, the risk of a lateral misalignment 113 (Fig. 6) of the displacement chamber access bores 103 with respect to the connections fastened to the outside of block 91, resp. the access bores thereof, is inevitable. Such a

misalignment leads to a slight canting of cartridge 101 (see Fig. 6). In the embodiments of the prior art provided with plane or alternatively with conical sealing surfaces of the access bores, this leads to a slightly irregular contact pressure along the sealing line since the sealing surfaces of the cartridge and of the access bore form a small angle between each other. Under the existing high pressures, this results in leaks or may even cause the seal to be pressed out in the direction of the opening of the angle.

As shown in Figs. 6 to 8, in order to solve this problem, one of the sealing surfaces of a junction is cambered, more particularly in a convex spherical shape, and the respective corresponding surface has a concave conical shape. In such a combination of the sealing surfaces, even if one of the sealing surfaces is inclined, i.e. if the longitudinal axis of the channel for the working medium extending therein is inclined with respect to that of the mating part, a circular contact line is still obtained, and thus also a substantially constant contact pressure. If the two contact surfaces are made of metal, a metallic sealing membrane is preferably interposed, preferably one of titanium because of its contact with the working medium, or of a synthetic material, particularly of PEEK.

In the example, the rounded sealing surfaces are provided on the connecting elements and on the displacement chambers and the conical ones on cartridges 102. However, the inverse arrangement is also possible. Furthermore, it is possible to use a sealing capsule 119, e.g. of PEEK, having rounded sealing surfaces on both sides (see Fig. 8: junction between a connection 100 and a simple cartridge 101).

In the same manner, the described construction also avoids leaks due to angular deviations between the parts to be joined.

According to a further preferred embodiment, in each junction, one 120 of the two sealing surfaces, or possibly both sealing surfaces in the case of two sealing surfaces with an interposed membrane, particularly metallic ones, may have steps 121 formed thereon (see Fig. 9). The result is a stepped sealing action or a plurality of line contacts, thereby further improving the sealing effect.

Another useful solution consists in providing concentric grooves 123 (Fig. 10).

A further preferred embodiment of the junctions for the connection of a capillary conduit without additional functions is shown in Figs. 12 and 13. Conduit 114 is made of titanium and is welded to an end piece 130. Connecting piece 100 is in the form of a threaded collar that is displaceable on the capillary conduit. The passage for conduit 114 through connecting piece 100 is enlarged at its inner end 132 to leave room for the weld seam 134. Sealing surface 136 of end piece 130 is designed as described above so as to ensure a perfect seal also in the case of a misalignment. In particular, the embodiment using a sealing capsule or the embodiment using a sealing membrane (see above) may be chosen. For the attachment of the conduit, the threaded collar is screwed into the pump enclosure in a known manner.

The contact surfaces 138 between end piece 130 and connecting piece 100 have complementary cambered, conical, or similar shapes to provide a self-centering action when the connecting piece is screwed into the pump enclosure.

However, contact surfaces 138 do not have a sealing function. Connecting piece 100 is made of PEEK or of steel.

Compared to the first described embodiment, this solution eliminates two sealing surfaces as well as the dead space caused by the channel in the empty cartridge, whose diameter is relatively large, and around the additional threaded collars screwed into connecting pieces 100.

Fig. 13 shows a connecting conduit 114 whose ends are provided with the above-mentioned connecting devices. Prior to the welding of the second one of end pieces 130, the two threaded collars 100 have to be slipped on conduit 114. The operation of bending conduit 114 to the required shape, e.g. the shape of a U, may take place afterwards.

While each one of the measures leads to in increased quality of the pump, they may also serve to simplify maintenance, i.e. particularly to reduce the skills required of the technician. Thus, in particular, maintenance can be carried out on site by the user without accepting losses in quality.

Further possible advantages follow from the description of the preferred embodiment:

Gradient capability down to 30 µl/min or less, particularly due to the reduced dead space (in the practical example: 9.45 µl vs. 36 µl in the prior art);
Increase of the operating pressure up to 1000 bar;
Possibility of providing cartridges 101, 102 with other or additional functions, e.g. for monitoring the flow rate or the operating conditions;
Safe and simplified assembly, resulting in easier maintenance; and/or

Possible application in high-pressure gradient systems where the mixing of the different components is effected in the high-pressure section.

The described exemplary embodiment enables those skilled in the art to find apparent modifications and complements without leaving the protective scope of the invention as defined by the claims. A number of such modifications have already been mentioned above. In addition, it is conceivable in the case of lower requirements to omit the adjusting capacity of the piston length or ball 25 for the accurate positioning of the hard material bars in sleeves 15, 16. However, such simplifications are more likely to be applied in the storage pump because of their smaller influence on the properties of the pump. It is also possible to use the inventive design of the sealing surfaces only in locations under operating pressure. Also conceivable is a pump having only one pump unit, i.e. only a feed pump, e.g. in applications where an accurate metering of small amounts of a flowable medium, more particularly a liquid is the only requirement (syringe or metering pumps).

Instead of being screwed in, the connecting elements may also be flanged to the pump body or fastened in another manner. However, they are preferably removable for uncomplicated maintenance and repair.

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